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THE HYDRONIUM ION ACTIVITY OF TRIFLUORO- AND TRICHLOROACETIC ACIDS[1]

CHARLES INMAN[2], WILLIAM BARRINGER[3], AND CONRAD E. RONNEBERG[4]

The relative activities of hydronium ions in aqueous solutions of trifluoroacetic (HA) and trichloroacetic (HB) acids as compared with the similar activities in dilute hydrochloric acid solutions have been determined by measuring the changes in the rates of hydrolysis of sucrose in the presence of the above acids. Numerous investigators have shown that the apparent monomolecular rate constant for the hydrolysis of sucrose is a direct function of the concentration of hydronium ions. The rate constants for the hydrolysis of sucrose have been measured for varying concentrations of hydrochloric, trifluoroacetic (HA) and trichloroacetic (HB) acids. The rate constants in dilute solutions of all these acids are the same, indicating that the levelling effect of water is great enough to make these acids all appear equally strong.

EXPERIMENTAL PROCEDURE

The rate constants were determined with a Kern polarimeter capable of being read to ± 0.05 degrees. A 20 centimeter tube was used with a sodium vapor light source. The sucrose solutions had a concentration of 10.000 grams per 100 ml of solution. Each solution had a known concentration of hydrochloric, trifluoro- or trichloroacetic acids. The sucrose and acid solution were brought to a temperature of 25.04° C. in a thermostat before mixing. After mixing, the polarimeter tube was filled, capped, and the initial polarimeter reading taken as quickly as possible. At the time of mixing, an electric clock was started. The time of the first reading was recorded. After the initial reading, the tube was kept in the thermostat except for the short time needed to get a polarimeter reading. The room temperature was usually about 25° C. It was assumed that temperature changes during the short time needed to make a polarimeter reading could be ignored. Each run required about eight hours. The tubes were then allowed to stand at room temperature (3–7 days) to get the final constant reading due to essentially complete hydrolysis. Two or more runs were made on each concentration of acid.

[1] Contribution from the Department of Chemistry, Denison University, Granville, Ohio. This research was aided by a financial grant by the Research Corporation, New York, N. Y. Financial assistance was supplied also by the Denison Research Foundation.

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The rate constant was calculated from the experimental data by using some form of the equation.

$$2.303 \log \left(\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f} \right) = kt,$$

or

$$\text{from a plot of } \log (\alpha_t - \alpha_f) \quad \text{against } t.$$

The resulting curve is a straight line. The slope of this curve permits a calculation of k, since

$$k = 2.303 \frac{\Delta \log (\alpha_t - \alpha_f)}{\Delta t} = 2.303 \times \text{slope}.$$

The solutions of trifluoroacetic acid were prepared by dilution of a very carefully fractionated sample of pure HA[5]. The acid was fractionated in a column a meter in length filled with glass helices equipped with a still head. A reflux ratio of about 20:1 was used. The fraction which was used distilled within a range of 0.1° C. The boiling point was 70.6° C. at 740 mm. The thermometer was checked against a thermometer calibrated by the Bureau of Standards. The various solutions of HA were made by volume and weight dilution of a solution which was 0.1033 N. The concentrations of the final solutions were always verified by titration.

The trichloroacetic acid was prepared from a pure commercial sample by distillation three times under reduced pressure. The product was kept in an evacuated desiccator over concentrated sulfuric acid for a week. The equivalent weight of the final product determined by titration with standard base was 163.93 (theoretical 163.40). The crystals are extremely hygroscopic. The discrepancy was ascribed to water picked up while weighing the sample. The various solutions of HB used in the rate experiments were made by weight and volume dilution of solutions of known normality. The concentrations of all solutions were verified by titration.

The solutions of hydrochloric acid used in the rate experiments were prepared as needed by dilution of a standard HCl solution. The final concentration was verified by titration.

The history of a typical rate experiment (Exp. No. 18) illustrates the procedure followed to obtain the rate constants: A fresh solution of sucrose was prepared by dissolving 20.000 g of sucrose in a 100 ml volumetric flask. 25.00 ml of this solution were placed in a 25.00 ml volumetric flask and placed in a thermostat maintained at 25.04° ± 0.03° C. Similarly, 25.00 ml of 0.1069 N HB were placed in the thermostat. In the meantime a 100 ml Erlenmeyer flask and the capped polarimeter tube were suspended in the thermostat. When all four were at bath temperature, the sugar and acid solutions were thoroughly mixed in the small Erlenmeyer flask. This solution was used to fill the polarimeter tube.

[5] Furnished by Minnesota Mining & Manufacturing Company, St. Paul 6, Minnesota.

TABLE 1

Run No. 18 0.05345 N HB

ELAPSED TIME MINUTES	αt	$\alpha t - \alpha f$	$\log (\alpha t - \alpha f)$
1.83	+13.20°	16.95°	1.2292°
30.2	+12.95	16.70	1.2227
62.1	+12.75	16.50	1.2175
99.2	+12.45	16.20	1.2095
160.8	+12.10	15.85	1.2000
218.0	+11.70	15.45	1.1889
285.2	+11.25	15.00	1.1761
344.8	+10.85	14.60	1.1644
394.2	+10.60	14.35	1.1568
454.6	+10.25	14.00	1.1461
510.5	+9.95	13.70	1.1367
α	−3.75		

The final solution contained 10.000 g of sucrose per 100 ml and 0.05345 N HB. At this time an electric clock was started. The tube was inserted in the polarimeter and the initial reading taken—in this case at 1.83 minutes. The tube was then placed in the bath. Special rubber caps were placed over the ends of the polarimeter tubes when placed in the bath. The tube was removed for a polarimeter reading at known intervals. The tube was then allowed to stand at room temperature six to seven days for the final polarimeter reading.

The data obtained in this run are shown in Table 1:

The data of Table 1 are shown graphically in Figure 1. The slope has value of 0.000184. Thus the velocity constant k for the hydrolysis of sucrose in the presence of 0.05345 N HB is 2.303 times greater or 0.000423 moles/min. The data on a check experiment gave a value for k of 0.000428 moles/min. The half-life for this reaction is 1640 minutes.

EXPERIMENTAL RESULTS

The rate constants for the runs using HCl, HA and HB acids are shown in Table 2.

The velocity constants in Table 2 are plotted against $c^{1/2}$ in Figure 2. From those curves values for k for a range of round concentrations for each acid were read. These are given in Table 3.

DISCUSSION OF RESULTS

The velocity constants for HA and HB were experimentally the same. The curves in Figure 2 indicate that the activities of solutions of HCl, HA, and HB are essentially the same in solutions with concentrations as high as c = ca. 0.06 N ($c^{1/2} = 0.24$). It was shown in a separate experiment that the hydrolysis of sucrose is not perceptibly influenced by B^- ions. A rate experiment made with 0.1841 N NaB, for example, showed no change in the polarimeter reading after

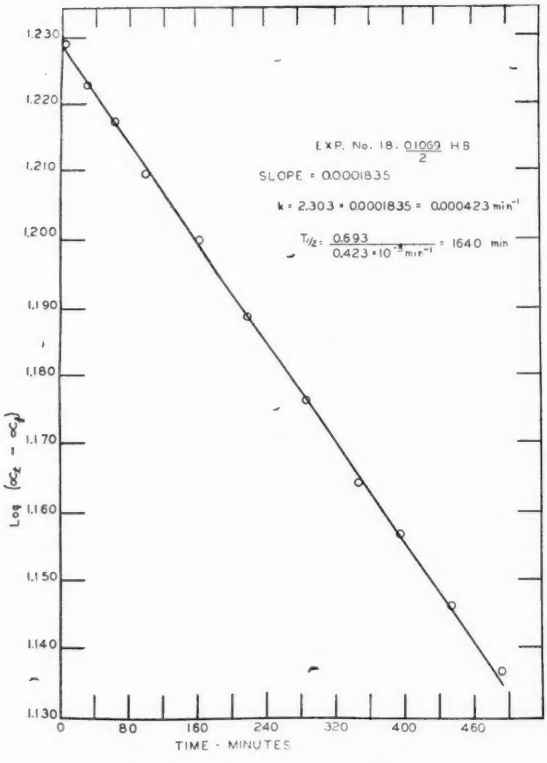


FIG. 1. Method Used to Evaluate Velocity Constants (k)

TABLE 2

CONC. HCl	NO. RUNS	k	CONC. HA	NO. RUNS	k	CONC. HB	NO. RUNS	k
0.5036N	6	.000532	0.4804	4	0.00349	0.1993	2	.00156
.2015N	4	.00186	.2000	4	.00153	.1075	2	.000845
.2001N	2	.00183	.1000	4	.000782	.07899	2	.000618
.1007N	2	.000857	.04940	3	.000379	.05344	2	.000436
.1000N	4	.000870	.0200	4	.000168	.02688	2	.000215
.07500N	2	.000629	.0100	5	.0000783	.01068	2	.0000828
.05525N	4	.000472						
.05055N	2	.000430						
.02548N	2	.000199						
.02000N	6	.000166						
.01005N	3	.0000760						
.01000N	6	.0000800						

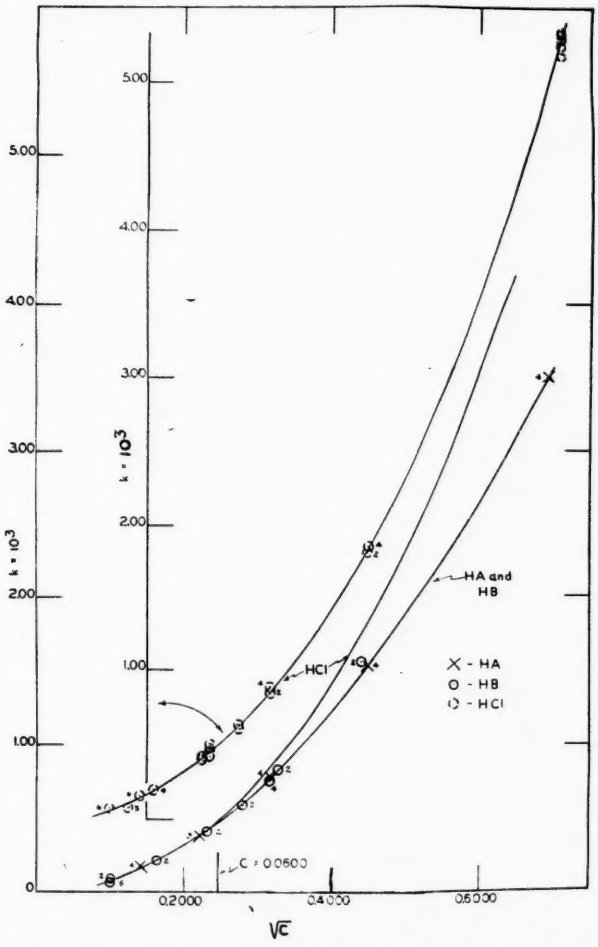


FIG. 2. Experimental Values for Velocity Constants (k) Plotted Against $\sqrt{c}$.

Note: The numbers beside each point on the graph indicate the number of experiments used to determine each point. The curve for HCl has been plotted twice, once with displaced ordinates, to increase the clarity of the curves.

over 400 minutes. There is no reason to believe the Cl^- or A^- ions have any influence on the rates of hydrolysis.[6]

The results indicate, therefore, that the acidity in water solutions appears to be the same for all three acids at concentrations of $c^{1/2}$ below about 0.24 N.

[6] Cf. G. Scatchard, *J. Am. Chem. Soc.*, *43*, 2387 (1921).

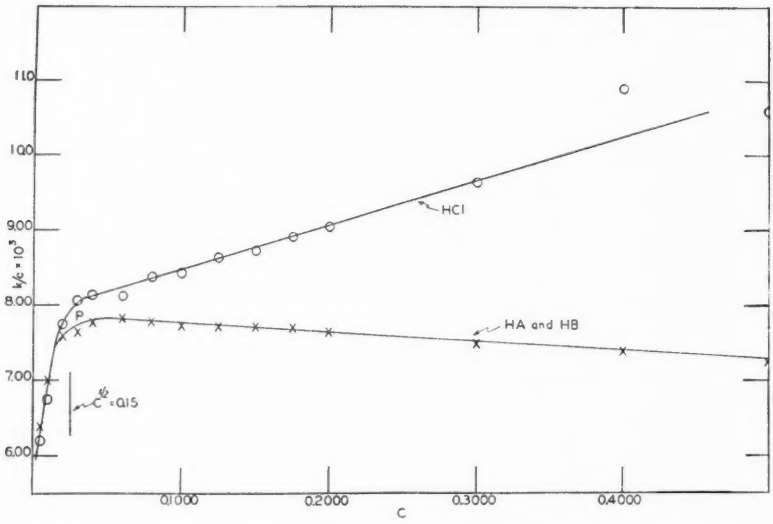


FIG. 3. Experimental Catalytic Ratios (k/c) Plotted Against Concentration (c).

TABLE 3

CONC. c	$\sqrt{c}$	k_{HCl}	k_{CF_3COOH} | k_{CCl_3COOH}	$(k/c)_{HCl}$	$(k/c)_{HA-HB}$
.00500N	.07071	0.000031	0.000032	0.0062	0.0064
.01000N	.1000	.0000675	.0000700	.00675	.00700
.02000N	.1414	.000155	.000155	.00775	.00760
.03000N	.1732	.000243	.000235	.00806	.00765
.04000N	.2000	.000325	.000311	.00813	.00778
.06000N	.2449	.000495	.000470	.00825	.00783
.08000N	.2829	.000670	.000620	.00838	.00779
.1000N	.3162	.000843	.000770	.00843	.00773
.1250N	.3532	.00108	.000965	.00864	.00775
.1500N	.3872	.00131	.00116	.00873	.00772
.1750N	.4190	.00156	.00136	.00891	.00771
.2000N	.4472	.00181	.00153	.00905	.00765
.3000N	.5477	.00289	.00225	.00963	.00750
.4000N	.6325	.00438	.00296	.0109	.00740
.5000N	.7071	.00524	.00362	.0106	.00721

The acidity is due to hydronium ions using the Bronsted-Lowry concept,[7]

$$HA + HOH \rightleftharpoons H_3O^+ + A^-.$$

The conversion to hydronium ions in the three solutions is quantitatively the same in water solutions, in concentrations where $c^{1/2}$ is less than about 0.24.

[7] Cf. J. N. Bronsted, *Chem. Rev.*, *5*, 231 (1928).

At concentrations above $c^{1/2} = 0.24$, the rate curves for HA and HB indicate a gradual decrease in hydronium ion activity as compared with HCl in the same concentrations. In 0.10 N and 0.15 N solutions of HA and HB, for example, the rate constants are about 9 and 12 per cent less than in HCl.

That the effect of HA and HB on the inversion of sucrose in concentrations greater than c = about .06 N is different from the effect of HCl is shown in Figure 3, where the catalytic ratios—the ratio of k/c—are plotted against c. If the effect of each acid on k was the same, the catalytic ratio should be the same. Likewise, if the effect is due to hydronium ions alone, the catalytic ratio should be constant. This would mean that the k/c vs. c curve should be a straight line intersecting the y axis at 90°. Inspection of the curves in Figure 3 show that this is not true. The break in the curves at $c^{1/2}$ = about 0.15 indicates two different effects at concentrations above and below the point P. Furthermore, the effect in solutions of HCl is different from that in solutions of HA and HB.

In the region below P, for all three acids, it is apparent that the catalytic ratio (k/c) increases rapidly with increase in c. If the change in k was due solely to change in concentration of hydronium ions, k should vary as c varies. Instead, k increases faster than c. This effect is independent of the acid in this range. The k_{HA} at 0.02 N is about 10 per cent larger than the value calculated on the assumption of a strict proportionality between k and c. This increase in the value of k over strict proportionality continues up to $c^{1/2}$ = ca. 0.15 (c = ca. 0.025).

Thus there is evidence that the presence of sugar increases the effect of the hydronium ions from the acid on the rate constant. This confirms observations reported by others.[8] Scatchard[9] estimated 10 grams sucrose per 100 ml of solution increased the value of a_{H^+} by 12 per cent. The change in $k_{0.02}$ experimental over $k_{0.01}$ is about 15 per cent greater than the calculated value on the assumption that k varies as c.

Thus it appears that the sucrose also has some effect on the activity of the acid in dilute concentrations. However, the effects seem to be the same as to HCl, HA, and HB, justifying the conclusion that these acids show the same behavior in dilute concentrations in water.

At values of c greater than 0.023, the shapes of the k/c vs. c curves show a change in character, and the effects are different in HCl solutions than for solutions of HA and HB. The values of $(k/c)_{HCl}$ continue to *increase* but at a distinctly slower rate. The values for $(k/c)_{HA\text{-}HB}$ remain nearly the *same* or slowly *decrease*. Thus there is evidence that both HA and HB, while both are strong acids, are distinctly different from HCl. It is only in solutions less concentrated than $c^{1/2} = 0.15$ that the three acids behave similarly.

The positive slope in the $(k/c)_{HCl}$ vs. c curve was interpreted as being due to a specific effect of the sucrose in increasing the activity of hydronium ions. Du-

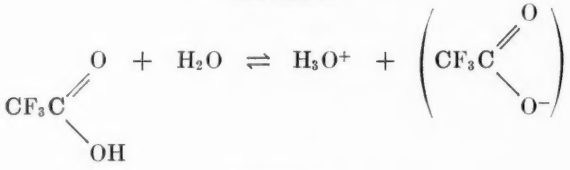
[8] Cf. G. Scatchard, *J. Am. Chem. Soc.*, *43*, 2387, (1921); C. M. Jones and W. C. McLewis, *J. Am. Chem. Soc.*, *117*, 1120 (1920); W. J. Taylor and R. F. Bomford, *J. Am. Chem. Soc.*, *125*, 2016 (1924); S. W. Pennycuick, *J. Am. Chem. Soc.*, *48*, 6 (1926).

[9] G. Scatchard, *J. Am. Chem. Soc.*, *45*, 1580, (1923).

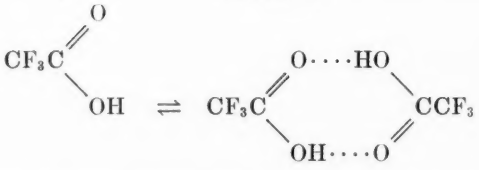
boux and Rochat[10] have reported that sucrose increases slightly the activity (6.6%) of hydronium ions in 0.1 m HCl solution containing 11.42 g sucrose per 100 ml of solution. Pennycuick[8] has shown that the rate of inversion of sucrose increases slowly during inversion (never more than 5%) indicating that sucrose specifically increases the activity of the added acid.

The curve for HA and HB in Figure 3, indicates that these acids in concentrations greater than $c^{1/2}$ = ca. 0.15 show significant differences from HCl. The effect of the sugar in increasing the activity of hydronium ions seems to disappear and the catalytic constant (k/c) ceases to increase or to even decrease. This can be accounted for on the assumption that the effects of dimerization due to hydrogen bonding begin to become noticeable. There is, apparently, a continuous competition between two tendencies, as indicated below:

PROCESS A



PROCESS B



It is believed that at concentrations less than $c^{1/2}$ = 0.15, that Process A predominates and both HA and HB behave as HCl. Apparently at concentrations above $c^{1/2}$ = 0.15, the process of association (B) occurs sufficiently to just offset the effect of the sugar in increasing the activity of the hydronium ions. The dimerization effect reduces the concentration of hydronium ions. Hence the catalytic ratio (k/c) remains nearly constant or even slightly decreases in the higher concentrations.

SUMMARY

The effect of the hydronium ions in solutions of hydrochloric, trichloroacetic, and trifluoroacetic acids on the velocity constants of inversion of sucrose have been measured in concentrations ranging from ca. 0.5 to 0.01 N. The results indicate that these acids are similar in very low concentrations, c less than ca. 0.06 N. Above this concentration the activity of the hydronium ions in trichloro- and trifluoroacetic acid is slightly less than in hydrochloric acid. The differences increase with concentrations. The catalytic ratios (k/c) are influenced by the presence of sucrose.

[10] M. Duboux and J. Rochat, *Hel. Chem. Acta*. 161–83 (1939).

THE ELECTROLYTIC CHARACTER OF TRIFLUOROACETIC ACID[1]

JOHN TRIMBLE[2] AND CONRAD E. RONNEBERG[2a]

The general acceptance of the Debye-Hückel-Onsager theory has made clear that the early values of ionization constants of many acids based upon conductance measurements cannot be accepted as reliable, if the interionic attraction effect was ignored in applying the Ostwald relationship, $K_I = C\alpha^2/1 - \alpha$. For example, the ionization constants for some halogenoacetic acids recorded in the literature are shown in Table 1.

The constants shown in Table 1 were based upon conductance measurements and in most of these interionic attraction effects were ignored in their evaluation. The exception is monochloracetic acid. By modern standards the values not starred cannot be considered reliable since interionic attraction effects have been ignored.[5] Redlick[6] presented evidence to show that equilibrium constants larger than about 0.2 cannot be determined reliably by conductance measurements. Kilpatrick has called attention to the unreliability of the ionization constant of trichloroacetic acid based upon conductance measurements.[7] Henne and Fox[8] have reported a value, based upon conductance measurements, of 0.588 for the ionization constant of trifluoroacetic acid, but with the qualification that the value by modern concepts is only an approximation. The theoretical difficulties involved in the determination of the K_I for trifluoroacetic acid have been discussed by Young and Jones.[9]

A number of investigators have given qualitative evidence that trifluoroacetic acid must be a very strong acid and comparable to hydrochloric acid.[10]

The equivalent conductances of dilute solutions of trifluoroacetic acid have been measured. The interpretation of the data in terms of the Debye-Hückel-Onsager theory indicates that it is a strong acid quite similar to hydrochloric

[1] Contribution from the Department of Chemistry, Denison University, Granville, Ohio. This research was made possible by a financial grant by the Research Corporation, New York, N. Y.

[2] Class of 1953, Denison University. Present address: Research Laboratory, Eastman Chemical Products, Inc., Kingsport, Tennessee.

[2a] Professor of Chemistry, Denison University.

[5] D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, *54*, 1429 (1932). T. Shedlovsky, A. S. Brown, and D. A. MacInnes, *Trans. Electrochem. Soc.*, *66*, 165 (1935). B. Saxton and T. W. Lauger, *J. Am. Chem. Soc.*, *55*, 3638 (1933).

[6] O. Redlick, *Chem. Rev.*, *39*, 333–56 (1946).

[7] Cf. M. Kilpatrick, *Annals New York Acad. Sci.*, *51*, 677 (May, 1949).

[8] A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, *73*, 2323 (1951).

[9] T. F. Young and A. C. Jones, *Annual Rev. Phys. Chem.*, *3*, 278 (1951).

[10] G. C. Finger and F. H. Read, *Trans.* Ill. State Acad. Sci., *29*, No. 2, 89–91 (1936). E. Gryskiewicz-Trochimoxski, A. Sporcynski, and J. Wink, *Rec. tra. chem.*, *66*, 419–26 (1949).

TABLE 1

Ionization constants of some halogenoacetic acids

HALOGEN	CH_2XCOOH	CHX_2COOH	CX_3COOH
Cl[3]	1.400×10^{-3}*	5×10^{-2} (?)	0.2 (?)
F[4]	2.20×10^{-3}	—	0.5 (?)

* Allowance made for interionic attraction effects.

acid. This conclusion has been verified by comparing the rates of hydrolysis of solutions of sucrose as catalyzed by trifluoroacetic and hydrochloric acids.[11]

The catalytic effect of the hydrogen ions in aqueous solutions of these acids are similar. Both the conductance and rate experiments indicate that trifluoroacetic acid is a very strong acid but strictly comparable to hydrochloric acid only in very dilute solutions.

EXPERIMENTAL PROCEDURE

A conventional Wheatstone bridge with high frequency current and a telephone receiver were employed to determine the conductances by the method of Kohlrausch. The recommendations of Jones[12] and Shedlovsky[13] were followed as far as practicable for the working precision desired in the final equivalent conductance values (0.4 per cent). The two segments of one arm of the bridge were in a Leeds and Northrup No. 4261 circular slide wire. The precision of reading was 0.2 per cent. The variable resistance in the other arm of the bridge was a Leeds and Northrup No. 4754 four dial a.c. resistance box with a limit of error of 0.05 per cent. A variable air condenser (50–1000 $\mu\mu f$ capacity) was used to balance out undesirable capacities in the conductance cell. A vacuum tube oscillator[14] was used to furnish frequencies of about 500, 1000, 1500, and 2000 cycles per second. The whole ensemble was suitably grounded.

The conductance cells were made of Pyrex and of the Washburn type.[15] The electrodes were lightly platinized. The cells were heavily coated with paraffin to prevent leakage effects. The cell constants were determined according to the recommendations of Jones and Bradshaw[16] using re-crystallized C. P. grade potassium chloride which was then carefully dried. The water used to prepare all solutions of potassium chloride was distilled water through which air freed of carbon dioxide and ammonia had been bubbled to bring it to a conductance minimum of about 1×10^{-6} ohms $^{-1}$ for a 1 cm. cube.[16] In the solutions of very

[3] *Int. Crit. Tables, VI*, 261 (1929).

[4] F. Swarts, *Bull. Acad. Rog. Belg. Classes des Science*, (3), 31, No. 6, 681–682 (1896); No. 6, 624–625 (1903); No. 6, 31–32 (1922).

[11] C. Inman, W. Barringer and Conrad E. Ronneberg, This Journal, Vol. 43, Art. 9, 175.

[12] G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, *50*, 1049 (1928).

[13] T. Shedlovsky, *J. Am. Chem. Soc.*, *52*, 1793 (1930).

[14] J. Mackus and V. Zeluff, "Handbook of Industrial Electronic Circuits," McGraw-Hill Book Company, Inc., New York, N. Y., 1948, p. 18.

[15] E. W. Washburn, *J. Am. Chem. Soc.*, *38*, 2431 (1916).

[16] G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, *55*, 1780 (1933).

TABLE 2

Equivalent conductances of solutions of trifluoroacetic acid

(1) c MOLES/LITER SOLUTION	(2) $\sqrt{c}$	(3) Λ OHMS^{-1}-CM^2 EQUIV.$^{-1}$	(4) $\Lambda - \Lambda_0$	(5) Λ HENNE AND FOX[19]
0.1500	0.3873	334	−56	—
0.1000	.3162	344	−46	342
0.07500	.2739	350	−40	348
0.05000	.2236	357	−33	356
0.02500	.1581	366	−24	366
0.01000	.1000	375	−15	375
0.005000	.07071	379	−11	380
0.0000	0.0000	(390)	0	(390)

low conductance, a correction was made for the conductance of the water. All measurements were made at 25.04 degrees C ± 0.02 degrees C.

In order to be sure that each resistance measurement was a true resistance, all measurements were made with at least two different resistances in the variable resistance box and with at least three different frequencies, usually 1000, 1500, and 2000 approximately cycles per second. This procedure follows the recommendations of Jones and Josephs.[12] Resistance measurements agreed to within 0.1 per cent or less.

Before making measurements with solutions of trifluoroacetic acid, the overall precision of the apparatus was verified by measuring the conductances of 0.07377 and 0.09884 N solutions of hydrochloric acid. The measured equivalent conductances agreed with those given by Harned within 0.2 per cent.[17]

The trifluoroacetic acid was a narrow boiling fraction from a kilogram sample[18] of pure trifluoroacetic acid. The boiling point was 70.6 degrees C (740 mm). The fraction which was used distilled within a range of 0.10 degrees C. The distillation column filled with glass helices was a meter in length surrounded with an evacuated jacket and wrapped in aluminum foil. By means of an adjustable still-head, distillation was conducted with a reflux ratio of 20:1.

RESULTS

Measurements of the conductances of solutions of trifluoroacetic acid were made in duplicate of the following concentrations—0.1532, 0.1023, 0.1006, 0.07536, 0.05014, 0.03391, 0.02829, 0.1039, 0.007727, 0.005390, 0.002489, 0.001070, and 0.001006 moles per liter of solution. The equivalent conductances at round concentrations read from a graph based upon all the data from the above measurements are given in Table 2.

Extrapolation of the Λ vs. $\sqrt{c}$ curve to zero concentration gave a value for $\Lambda_0 = 390$ ohm^{-1} cm^2 equiv.$^{-1}$. Henne and Fox[19] reported the same value. The

[17] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 537.

[18] Donated by Minnesota Mining and Manufacturing Company, St. Paul, Minn.

[19] A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, *73*, 2323 (1951).

limiting slope is 150. The limiting value for Λ_0 is in agreement with the theoretical slope $(A + B\Lambda_0)$, which is 150.

The Debye-Hückel-Onsager theory relates the fraction ionized to the conductance as follows:[20]

$$\Lambda_e = \Lambda_0 - (A - B\Lambda_0)\sqrt{c\alpha} = \Lambda_0 - (A + B\Lambda_0)\sqrt{c\Lambda/\Lambda_e} \qquad \text{Eq. 1}$$

Λ_e is the equivalent conductance of the hypothetical completely ionized electrolyte at any given concentration. By trial and error, a value for a given pair of c and Λ values in Table 2 can be calculated. For example, when $c = 0.1000$, $\Lambda = 343$, Λ_e was found to be 346. The fraction dissociated at this concentration is 343/346 or 0.993. This analytical procedure applied to all the data in Table 2 gave values for the fraction ionized in solutions of trifluoroacetic acid closely approaching unity, indicating essentially *complete dissociation* as in the case of hydrochloric acid.

The limiting Debye-Hückel-Onsager equation for a strong 1:1 electrolyte in dilute solutions[21] is,

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} \qquad \text{Eq. 2}$$

Onsager[22] has shown that the Λ vs. $\sqrt{c}$ curves for strong 1:1 electrolytes should approach the limiting conductance curve from *above*, while incompletely dissociated electrolytes must approach the limiting curve from *below*. If trifluoroacetic acid is not completely dissociated as has been reported in chemical literature, Equation 2 must be corrected due to incomplete dissociation. In dilute concentrations,

$$K_I = \frac{(\alpha f)^2 c}{1 - \alpha}. \qquad \text{Eq. 3}$$

In very dilute solutions $f \cong$ unity and $\alpha^2 c \cong c$. Hence,

$$1 - \alpha = c/K_I. \qquad \text{Eq. 4}$$

The decrease in conductance, then, due to incomplete dissociation is $\Lambda(1 - \alpha)$, which approaches $\Lambda_0(1 - \alpha)$ near infinite dilution. This leads to the equation of Onsager for the conductance of an electrolyte which is largely but not completely dissociated[23]

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} - \frac{\Lambda_0 c}{K_I}. \qquad \text{Eq. 5}$$

The effect of the term $\Lambda_0 c/K_I$ in Equation 5 for electrolytes not completely dissociated is to bring the conductance curve *below* the limiting curve. In Figure 1, $\Lambda - \Lambda_0$ values from Table 2 are plotted against $\sqrt{c}$. The dashed line gives the

[20] Cf. S. Glasstone, "Textbook on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 907.

[21] S. Glasstone, *ibid.*, p. 905.

[22] L. Onsager, Physik. Z. *28*, 277 (1927).

[23] Cf. H. S. Harned and B. B. Owen, *ibid.*, p. 145.

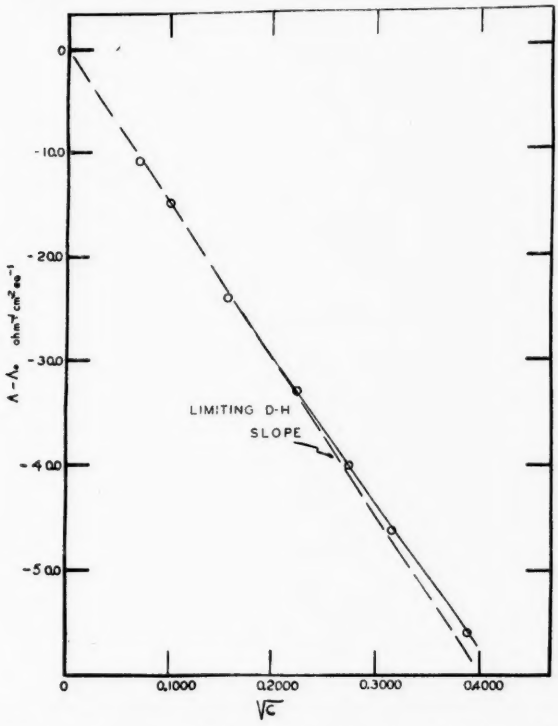


FIG. 1. Experimental Values for $\Lambda - \Lambda_0$ Plotted Against $\sqrt{c}$

theoretical limiting Debye-Hückel slope ($A + B\Lambda_0$). Since the curve approaches the limiting curve from above, it appears that trifluoroacetic acid in very dilute solutions is completely dissociated and cannot have a finite ionization constant.

Equation 2 is the limiting quantitative conductance equation for very dilute solutions of 1:1 strong electrolytes according to the Debye-Hückel-Onsager theory. In solutions of appreciable concentration where this equation does not strictly apply, we can solve for the "apparent equivalent conductance Λ_0'." This is obtained by solving Equation 2 for Λ_0 and designating it Λ_0'. Hence,

$$\Lambda_0' = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}}. \qquad \text{Eq. 6}$$

Values for Λ_0' for trifluoroacetic acid computed from the data in Table 2 are plotted against $\sqrt{c}$ in Figure 2. Values for Λ_0' for hydrochloric acid[24] are included.

In very low concentrations where interionic attraction effects are absent or negligible, the apparent and limiting conductance become identical and the limiting curve is perpendicular to the y-axis. It is apparent from Figure 2, that both

[24] Data of T. Shedlovsky, *J. Am. Chem. Soc.*, *54*, 1411 (1932).

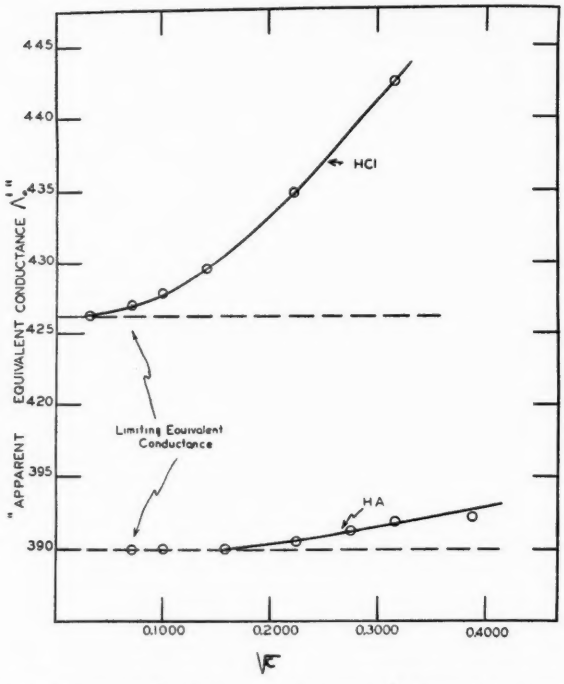


FIG. 2. "Apparent Equivalent Conductance Λ_0'" Plotted Against $\sqrt{c}$

curves approach the limiting conductance curve asymptotically from *above*—a criterion for complete dissociation.[22] While the conductance curve for trifluoroacetic acid approaches the limiting slope from *above*, it is apparent that the interionic attraction effect is much less than for hydrochloric acid. This is believed to be due to the relatively large size of the trifluoroacetate ion. The effective diameter of the hydrated anion has been estimated to be 4.5 Å.[25] Bjerrum[26] has pointed out that 1-1 electrolytes in water with values of apparent ionic diameter (a^0) greater 3.5 Å should be strong electrolytes.

The interatomic distances in the CF_3COO^- ion have been measured. The C-F and C-C distances have been shown to be 1.36 Å and 1.47 Å, respectively,[27] as compared with the C-Cl distance of 1.76 Å in trichloroacetic acid and a C-C distance of 1.54 Å in acetic acid. These effects are attributed to the small size and extreme electro-negativity of the fluorine atom.[28] It is reasonable to believe, therefore, that the CF_3COO^- ions are highly hydrated through hydrogen bond-

[25] A. J. Kielland, *J. Am. Chem. Soc.*, *59*, 1675 (1937).

[26] N. Bjerrum, KgC. Daiske Vidensk Selskof, I, No. 9, (1926).

[27] J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, *66*, 574–584, (1944).

[28] Cf. R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," John Wiley and Sons, Inc., New York, N. Y. (1951).

ing. This fact coupled with the large mass of the ion would account for its relatively low equivalent conductance (40.0 ohm^{-1} cm^2 $equiv.^{-1}$). The limiting ionic conductance of chloride ion is 76.34 ohm^{-1} cm^2 $equiv.^{-1}$. The reduced interionic attraction effect of the CF_3COO^- ion can be attributed to the relative large size of this ion due to hydration.

SUMMARY

The equivalent conductances of solutions of trifluoroacetic acid have been measured in the range $C = 0.005$ N to $C = 0.15$ N. The limiting conductances—below c = ca. 0.02500 N—are proportional to $c^{1/2}$ as demanded by the Debye-Hückel-Onsager equation for a strong electrolyte. The limiting slope of the Λ versus $c^{1/2}$ curve is that called for by the Debye-Hückel-Onsager equation. The evidence indicates that trifluoroacetic acid in very dilute solutions is entirely dissociated and comparable to hydrochloric acid. The interionic attraction effects, however, are less than in the case of hydrochloric acid, presumably due to the larger size and the greater degree of hydration of the trifluoroacetate ion. The leveling effect of water is great enough to make trifluoroacetic acid in water as strong an acid as hydrochloric acid. Trifluoroacetic acid does not have a measurable ionization constant in water solution.

RECALL OF EXPERIENCES AS A FUNCTION OF INTENSITY AS COMPARED TO QUALITY (PLEASANTNESS OR UNPLEASANTNESS) OF FEELING TONE[1]

JOHN A. BARLOW[2]

Spencer in 1873 formulated a "pleasure-pain theory of learning" according to which a pleasant feeling is a feeling we seek to bring into consciousness, and an unpleasant feeling is one which we seek to get out of consciousness. In 1901 Freud presented his theory of repression. According to Freud, forgetting is sometimes the result of a person's attempt to avoid memories that are painful to him.

These two theories plus Thorndike's formulation of his original "law of effect" have stimulated a very considerable amount of research on memory for pleasant as opposed to unpleasant experiences.

In 1936 Shaffer reviewed the evidence to that time and concluded that "Experiments that more nearly reproduce real life situations involving the retention of personal experiences show the forgetting of the unpleasant in most striking degree" (p. 214).

The traditional procedure in studies of memory for pleasant and unpleasant experiences is to ask subjects to record their most pleasant experiences of the past few days, and then their most unpleasant experiences for the same period. After an interval of several days or weeks the subjects are asked to report the same experiences a second time. The percentage of the initially recorded pleasant experiences forgotten during the interval is then compared to the percentage of the unpleasant experiences forgotten.

Turner and Barlow (1951) reported a study which casts considerable doubt on the validity of the interpretation given to previous studies. These investigators followed the traditional procedure except in one respect. One group of their subjects reported pleasant experiences first as in previous studies. For a second group of subjects unpleasant experiences were reported first. Turner and Barlow conclude that "When pleasant experiences were recalled first, a higher percent of pleasant experiences was recalled. The number of responses made . . . differed significantly. When the factor of temporal sequence in recall was minimized by using a counter-balanced order, there was little difference found in the ability to recall pleasant as opposed to unpleasant experiences."

Quite opposed to the Spencer-Freud point of view is a theory suggested by D. E. Cameron (1947). Cameron's formulation states that "The more intensely an individual reacts to a situation . . . the more will be remembered."

[1] This research work was completed while the author was serving as an instructor at the Georgia Institute of Technology. A paper based on this material was read at the meetings of The Southern Society for Philosophy and Psychology, April, 1952.

[2] Assistant Professor of Psychology, Denison University.

TABLE 1

Retention as a function of degree of intensity

RANK	FIRST RANKING		SECOND RANKING	
	Number of Experiences	Number Forgotten	Number of Experiences	Number Forgotten
1	32	6 (19%)	32	1 (3%)
2	32	4 (12.5%)	32	5 (16%)
3	32	9 (28%)	32	10 (31%)
4	32	12 (37.5%)	32	13 (41%)
5	32	15 (47%)	32	17 (53%)

Koch (1930) pointed out that both pleasant and unpleasant experiences are better remembered than neutral experiences. Meltzer (1930), Cason (1932), and Menzies (1935) all observed that the more pleasant or the more unpleasant an experience was the better the recall.

Waters and Leeper (1936) had their subjects rate the experiences on a three point scale of intensity. They report that "frequency and extent of recall for ordinary life experiences appear to be correlated with intensity of feeling-tone rather than quality of feeling-tone."

Turner and Barlow (1951) had some of their subjects rank their experiences, both pleasant and unpleasant, on a single continuum from most intense to least intense and report that: "Recall was found to be a function of intensity of the experience, whether pleasant or unpleasant."

The present study differs in the following respects: (1) obtaining an equal sample of experiences from each subject, instead of permitting the number of experiences reported by a subject to vary say from three experiences reported by one subject to eighteen reported by another; (2) having the subjects re-rate their experiences at the time of second recall and reporting forgetting as a function of both of these sets of ratings taken separately; (3) having the subjects themselves decide whether an experience reported at the time of second recall was the same experience reported differently or whether the original experience had actually been forgotten; (4) controlling primacy of report for pleasant as opposed to unpleasant experiences was controlled by having the subjects record their five experiences prior to any mention of intensity or affect.

TABLE 2

Retention as a function of quality of feeling tone

QUALITY	FIRST RATING		SECOND RATING	
	Number of Experiences	Number Forgotten	Number of Experiences	Number Forgotten
Pleasant	74	19 (26%)	73	16 (22%)
Neutral	16	8 (50%)	29	14 (48%)
Unpleasant	70	19 (27%)	58	16 (28%)

PROCEDURE

Thirty-two students at Georgia Tech each reported five "emotionally toned" experiences of the past week. They then ranked these experiences by intensity and specified quality of feeling tone. Fifteen days later the students were asked to recall the same experiences a second time. The initial reports from the first recall were then returned, correct recalls specified, and the experiences re-rated in line with feeling at the time of this second recall.

RESULTS

Table 1 presents an analysis of retention of the experiences as a function of reported degree of intensity at time of first recall and time of second recall. Percentage of experiences reported which are recalled a second time fifteen days later appears to be a clear function of reported intensity of the experience with a somewhat smoother trend using the second ranking.

Table 2 presents an analysis of retention of the experiences as a function of reported quality of feeling tone. As in previous studies a smaller percentage of both pleasant and unpleasant experiences are forgotten than of neutral experiences. The percentage of unpleasant experiences forgotten is slightly greater than that of pleasant experiences on both ratings. In the Turner and Barlow study there was a similar small difference with a larger percentage of the pleasant experiences being forgotten.

CONCLUSION

It appears that memory of every day experiences is a function of intensity of feeling tone about the experience. There is little evidence to support the position that memory for such experiences is a function of whether they are remembered as pleasant or unpleasant.

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ELECTRIC SHOCK VS. FOOD DEPRIVATION AS MOTIVATION IN PSYCHOLOGICAL EXPERIMENTATION

JOHN A. BARLOW[1]

Yerkes (1907, pp. 98–100) pointed out certain advantages of using "punishment instead of reward as the chief motive." Specifically, Yerkes refers to electric shock with shock termination as the reinforcement as opposed to deprivation of food followed by food as reinforcement in learning studies. Yerkes' objections to the use of "hunger" or other deprivation as motivation are "the discomfort of the animal and the impossibility of keeping the motive even fairly constant."

It is obvious that in cases where deprivation is to motivate the animal during the experiment, the animal must be deprived for most of the time during which the experimental schedule is being carried out (and this may be, and often is, several weeks). In experiments using some noxious stimulus, such as electric shock, the animal is motivated only during the relatively brief period each day during which experimentation is carried on. With deprivation, the animal is necessarily motivated for long periods when it is not under observation; with shock, the animal is highly motivated in general only while under observation. We have observed that, at least in consideration of the several laboratories with which we are familiar, a good many more experimental subjects have died of deprivation than have been killed as a result of over stimulation.

Current feeding schedules give greatly improved techniques and the possibility of keeping amounts of deprivation fairly constant. However, the considerable introductory scheduling and precise timing necessary invite occasional slips unless great care is exercised. The most obvious indication that motivation is not constant from animal to animal is the greater variability in performance reported in studies of animals motivated by food deprivation as compared to those motivated by electric shock. However, experimental studies actually comparing various types and lengths of deprivation and types and strengths of noxious stimulation are unfortunately not available at the present time.

Aside from the continuing pertinence of such arguments as those originally introduced by Yerkes, there are certain rather obvious advantages to shock motivation in studies within the currently important areas of secondary motivation and secondary reinforcement and the parameters involved in their genesis.

An electric shock has a relatively precise onset and termination. If hunger has any specific onset, we are still so far from knowing when this would be that seemingly no one has even previously formulated the question. As for the termination of hunger: here a considerable amount of research and conjecture is available. However, the matter is certainly still an open question. The problems

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this situation introduces in studying secondary reinforcement are exemplified in a study by Schoenfeld, Antonitis and Bersh (1950). In this experiment the stimulus which was to acquire reinforcing properties was presented to rats in a Skinner Box during their eating of the food pellets. After one-hundred reinforced trials (bar pressing—food pellet—eating of food and occurrence of stimulus) no significant effect was found, i.e. the stimulus which had accompanied eating apparently had not acquired properties of secondary reinforcement.

Miller (1951) reviews twenty-one studies of "learned reward based on hunger and food", but not a single study of learned reward based on electric shock and shock termination. Since this time we are aware of only three such studies: Coppock (1951), Barlow (1953), Smith and Buchanan (1954).

In summary, we would conclude that: (1) electric shock is more humane than food deprivation; (2) it is possible to control level of motivation more accurately with shock; (3) the dearth of studies of secondary reinforcement based on shock termination is very unfortunate in view of the greater control and specification of variables possible.

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